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COATINGS

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SiC – Si_3N_4 – SiO_2 HIGH-TEMPERATURE COATINGS FOR METAL FIBER SEALING MATERIALS

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The results of developing thin-film ceramic coatings for metal fiber sealing materials are presented. Their technological and physical-mechanical properties at temperatures 700, 800, 900, and 1100°C have been investigated.

Key words: ceramic-forming polymer, polycarbosilane, polysilazane, metal fiber sealing material, amorphous boron, cobalt sulfate, thin-film coating.

To improve the cost-effectiveness, reliability, and service life of aviation gas-turbine engines (GTEs), which are promising power plants for aircraft, fundamentally new high-temperature materials must be developed, specifically, abradable sealing materials, on order to decrease the losses through the gaps between the disks and blades of the compressor and turbine at temperatures above 800 – 1000°C. Fundamentally new sealing materials have been developed at VIAM. They consist of discrete metal fibers of the systems Ni – Cr – Al, Ni – Cr – Al – Y, and Fe – (Ni) – Cr – Al – Y for working temperature of the compressor and turbine of the GTE from 700 to 900°C. The advantages of the new sealing materials are low density (≤ 1.8 g/cm^3), high porosity (65 – 90%), high erosion resistance (≥ 1100 units) and very high abradability (10 : 1), which ensures that the wear of the compressor blades will be 2 or 3 times lower and the mass of the sealing material will decrease by up to a factor of 5 [1].

It is shown in [2 – 3] that the performance of the metal fiber sealing materials can increase considerably if a special coating that modifies the surface of the fibers and at the same time protects them from the effects of high temperatures is deposited on the surface of the fibers. The use of such coatings can be regarded as a method of increasing the heat-resistance and structural characteristics of metal fiber materials.

The basic work in this field is associated with the development of protective multilayer composite materials which include intermetallide corrosion-resistant layers made of nickel and chrome and external cover layers made of glass, ceramic, and metal-ceramic. The compounds SiO_2, TiO_2, Al_2O_3, MgO, SiC, Si_3N_4, and finely dispersed Al powder are used as the basic components of the coatings. The maximum working temperature of the abradable coated sealing materials developed can be no higher than 1000°C.

The objective of the present work was to investigate the possibilities of increasing the working temperature of porous fiber sealing materials based on metal fibers of the system Fe(Ni)CrAlY to 1100°C by using high-temperature thin-film coatings having high phase stability at high temperature and consisting of nanosize particles of silicon oxide, carbide, and nitride obtained by pyrolytic decomposition of ceramic-forming polymers.

Considering the small size of the discrete metal fibers of the sealing materials (fiber diameter 5 μm, length to 1 mm), one of the main requirements for the new coatings is to create nanosize defect-free thin films which are uniformly distributed on the entire surface of a fiber and possess high wettability power and bonding with the fiber.

The main research problem was to develop the coating composition and the technology for synthesizing multicomponent amorphous systems with a high degree of uniformity and purity as well as to obtain spatially organized structures with nanometer sizes, which will make it possible to impart to the new thin-film coatings a unique system of physical-chemical and mechanical properties. The realization of this problem was made possible by choosing the type of organosilicon polymer, modifying fillers, and their heat-treatment

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regimes in order to maximize the yield of the ceramic remainder (not less than 75%). This made it possible to obtain an ultrathin protective coating layer consisting of nanosize silicon carbide, nitride, and oxide particles with minimum porosity. The ultrathin protective layers of the coatings increase the high-temperature strength of the alloy by 150 – 200°C, preserve the initial structure of the porous sealing material, abradability, and durability. The density of the material increases by no more than 5%.

Thin-film coatings were synthesized using precursors based on polycarbosilanes and polysilazanes, which as a result of solidification and pyrolysis in an inert medium form a ceramic residue consisting of a mixture of SiC, Si_3N_4, and SiO_2. These precursors based on ceramic-forming polymers combined with ceramic and glass-forming fillers make it possible to synthesis thin-film polyfunctional protective coatings. To increase the high-temperature strength and heat-resistance and to improve the technological and protective properties of thin-film coatings, modifying components possessing glass-forming properties and improving the adhesion of ceramic coatings were added to coating compositions.

The ceramic forming polymer of polycarbosilane PKS-21M and modifying components — powders of amorphous boron B_{am} and cobalt sulfate — were investigated as initial components. An advantage of the ceramic-forming polymer PKS-21M is that at least 75% ceramic phase SiC – Si_3N_4 – SiO_2 is obtained. Thin-film coatings are effective because the temperature at which they are formed is low — 700°C, much lower than the working temperature of the sealing material (900°C), and the phase stability of the amorphous structure of a coating is high. The main function of the modifiers is to eliminate defects which appear in the coatings during formation and operation.

The preparation of the bonding polymer PKS-M and modifying components included an evaluation of their technological properties: aggregate state, particle size range, solid-phase content, and moisture content. A high content of moisture and volatile substances in the materials is the reason why defects appear in the finished articles. A low content of solvent can result in reduced fluidity of the material and a nonuniform coating distribution over a fiber surface. An important property of modifying components is their particle size range. Fillers consisting of large particles can become nonuniformly distributed in course of deposition and formation of a coating. Fillers must have comparably small particle sizes and become uniformly distributed in the volume of the ceramic composite materials. To achieve stable results from testing the properties of the initial components and suspensions of the precursors based on ceramic-forming polymers, the studies were performed on three batches of each component of the suspensions of the precursors.

To determine the properties of the PKS-21M polymer, amorphous boron and cobalt sulfate powders and preparatory working solutions and suspensions of the precursors were chosen as follows: the aggregate state of the substances was determine according to GOST 208411, the solid phase of the polymer was determined by a weighing method based on attainment of a constant mass of the substance with heating to 140°C (GOST 17537), the moisture content of the powder was determined according to GOST 9758, the conventional viscosity of the suspensions of the precursors was determined with a VZ-246 apparatus (GOST 8420), the dispersity expressed in terms of the specific surface area of the particles S_{sp} (m^2/kg) was determined on the Analizette-22 apparatus, and the density was determined with a hydrometer (GOST 18481–81).

In its initial state the experimental polymer consisted of uniform dark-brown fragments without mechanical inclusions, the mass content of the solid phase was 72 – 75%, amorphous boron B_{am} consisted of a uniform free-flowing black power, the dispersity of the particles S_{sp} = 980 – 1050 m^2/kg, the moisture content of the powder was 3%, the cobalt sulfate $CoSO_4$ was a uniform rose-colored free-flowing powder, S_{sp} = 700 – 780 m^2/kg, and the moisture content was 5%. The quality evaluation of the precursor suspensions included a determination of the content of the solid phase, the conventional viscosity, and the density.

The effect of the grinding time of the modifying components B_{am} and $CoSO_4$ on the dispersity S_{sp} of the powders and the effect of the drying regimes on their moisture content were investigated. It was established that increasing the grinding time from 10 to 40 h increases the specific surface area of the powders. The grinding time for the modifying components was determined: amorphous boron B_{am} — 20 h, S_{sp} = 1530 – 1560 m^2/kg; cobalt sulfate $CoSO_4$ — 30 h, S_{sp} = 1300 – 1400 m^2/kg. The drying regime for amorphous boron and cobalt sulfate giving a moisture content of the powders less than 1% was determined to be ±150°C, 1 h. It was established that as the content of the modifying additives B_{am} and $CoSO_4$ increases, the concentration of the solid phase, the conventional viscosity, and the density increase in proportion to the amount of the fillers introduced: the content (wt.%) of the solid phase of the precursors from 72.6 to 77%, the conventional viscosity from 20 to 35 sec, and the density from 660 to 770 kg/m^3.

The experimental precursors based on ceramic-forming polymers were used to create experimental samples of thin-film coatings. The characteristic feature of the technological process of obtaining thin-film coatings from polymer precursors is solid-phase synthesis of a ceramic layer of the system SiC – Si_3N_4 – SiO_2 on the surface of the fibers throughout the entire volume of the material.

The thin-film coatings formed in several stages: low-temperature gel-formation, low-temperature solidification, and low- and high-temperature solidification. After solidification the samples were subjected to pyrolysis. The coating was obtained in an inert medium at atmospheric pressure. The yield of the pyrolytic residue with the composition SiC – Si_3N_4 – SiO_2 was 83 – 89%.

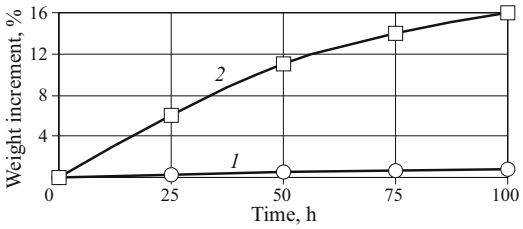

Fig. 1. High-temperature strength of samples of abrasion-resistant sealing material Fe(Ni)CrAlY with a thin-film coating at test temperature 1100°C.

The properties of the thin-film coatings were studied on samples of durable sealing material consisting of metal fibers of the alloy Fe(Ni)CrAlY. The experimental compositions of thin-film coatings were deposited on 40 × 15 × 5 mm samples.

Two methods of depositing a thin-film coating were used in this study: free and vacuum permeation of three-dimensional frameworks consisting of metal fibers. The permeation with a thin-film coating (with the solution PKS-21M with modifying additives $B_{am} + CoSO_4$) required from 1 to 3 h. The fibers were permeated in two stages. The deposition quality of a thin-film coating was evaluated according to the density of the samples obtained. It was determined that the optimal time of each deposition cycle for a thin-film coating on the samples was 1 h for the free permeation method and 0.5 h for the vacuum method. Both methods are acceptable and make it possible to obtain equivalent density of the samples 1.9 – 1.95 g/cm^3.

Two formation regimes for a thin-film coating were studied. A thin-film coating was formed as a result of pyrolytic decomposition of a ceramic-forming polymer in an inert medium at temperatures 700 – 900°C in 1 – 3 h and 950 – 1000°C in 0.5 – 1.5 h. After the coating formed, the density of the samples was 1.95 – 2 g/cm^3 with a stable and uniform coating structure.

The studies of the technological formation parameters of a thin-film coating lead to the optimal technological scheme for obtaining a coating. This scheme includes two-stage permeation of the three-dimensional framework consisting of metal fibers of the solution of PKS-21M with modifying additives $B_{am} + CoSO_4$ and post-permeation drying of the samples in air. This technological scheme for fabricating a thin-film coating made it possible to obtain samples with stable and minimum density 1.9 g/cm^3.

The thin-film coating technology was optimized by studying the effect of the scale factor on the formation process for such a coating. Three-dimensional frameworks made of metal fibers with the dimensions 40 × 51 × 5 and 120 × 45 × 5 mm were used. The effect of the scale factor of the samples made of metal fibers on the infiltration, drying, and formation of a thin-film coating was investigated. The criterion for evaluating the effect of the scale factor was the density of the samples of the sealing material. It was determine that when the dimensions of the samples are tripled, the permeation time must be tripled — from 1 to 3 h, the drying time must be increased by a factor 1.5 — from 15 to 24 h, and the formation time for permeation in a vacuum furnace at 700°C must be doubled from 1 to 2 h.

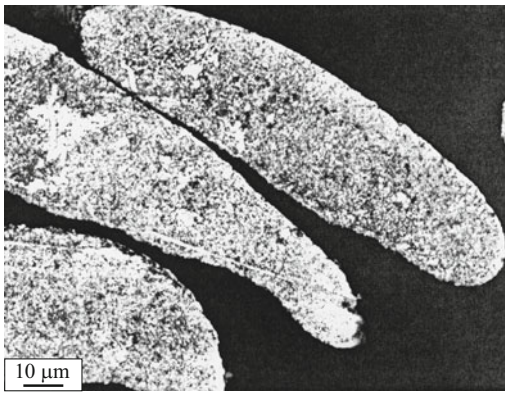

Fig. 2. Morphology of samples (×1000) of sealing material with a thin-film coating at testing at temperature 1100°C for 100 h.

The optimal technological scheme was used to prepare sample for studying the high-temperature strength, heat-resistance, corrosion resistance, and abradability of porous materials made of fibers of the alloy Fe(Ni)CrAlY with a thin-film coating.

Figure 1 shows the high-temperature strength of porous materials made of fibers of the alloy Fe(Ni)CrAlY with a thin-film coating.

The use of a thin-film coating for abrasion-resistant metal fiber sealing material Fe(Ni)CrAlY ensures that it will be serviceable at 1100°C for 100 h without breaking down, while without the coating the sealing material becomes unserviceable and breaks down as a result of strong oxidation.

The high anti-oxidation resistance of the thin-film coating is due to the formation on the surface of the thin discrete metal fibers ($d_f = 5$ μm, $l = 0.5 – 1$ mm) of a continuous glass-ceramic film consisting of a material from the system $SiC – Si_3N_4 – SiO_2$, possessing high adhesion to the fibers.

The introduction of ultradisperse amorphous boron powder in the amounts 1 – 3% made it possible to expand substantially the temperature interval of coating serviceability and lower the oxidizability of the material at the early stages of heating by the formation of a glass phase containing B_2O_3. The introduction of cobalt sulfate made it possible to increase the strength of the adhesion of the coating with the metal fiber, lower the porosity of the protective layer, and increase it high-temperature strength at high temperatures (1100°C).

Figure 2 shows the morphology of samples of sealing material comprised of discrete metal fibers with a thin-film coating after testing at temperature 1100°C for 100 h.

The samples of the new durable sealing material also remain intact during the thermocyclic tests.

Fig. 3. Exterior view of samples of porous durable material with a thin-film coating after testing for oxidizability and heat-resistance.

Figure 3 shows an exterior view of the samples of durable material comprised of discrete metal fibers with a thin-film coating after testing for oxidizability and heat-resistance. The coating on the samples is tight with no cracks and is uniformly distributed through the entire volume of the fiber.

Principal Technical Properties of Sealing Material Fe(Ni)CrAlY with Thin-Film Coating*

Density, g/cm^3:	
no coating	≤ 1.85
with coating	≤ 1.9 – 2.0
Working temperature, °C:	
no coating	900
with coating	1100
Abradability (ratio of wear of the sealing material to wear of the material at the blade end with cut-in) at temperature 1100°C:	
no coating	Material unserviceable
with coating	5 : 1
Heat-resistance (temperature drop 1100 – 20°C, duration of one cycle 1 min), cycle:	
no coating	Not determined
with coating.	100 without break down

* V. P. Migunov and D. P. Farafonov participated in the work.

The heat-resistance of the coated sealing material was investigated on 50 mm in diameter samples soldered to a metal substrate consisting of VZh-101alloy followed by permeation with a precursor suspension and formation of a coating at 700°C. The samples were heated to 1100°C and then cooled to room temperature; the number of heating changes was 100. All samples passed the test without break down or cracking, which shows that the heat-resistance of the coating is high.

The abradability was studied on a sample with the dimensions 75 × 50 × 5 mm. The testing procedure was based on measuring the wear during contact between samples comprised of the sealing materials and compressor blade material as they approached one another by a prescribed amount and at a prescribed velocity, modeling the processes occurring in engines. The abradability tests showed that the maximum groove depth in the experimental material is 0.4 – 0.5 mm with abradant wear from 0.1 to 0.2 mm on average. The abradability is (2 – 5) : 1, which is good at high temperatures (to 1100°C).

The erosion resistance of the fiber sealing material with a thin-film coating was determined by the method used to study the operational properties of MM 1-595-3-147–2002 in the following testing regime: angle of attack 30°, air pressure 0.49 MPa, corundum grain size 10 μm, and volume of electrocorundum 5 cm^3. The results of testing the sealing material with a thin-film-coating for erosion resistance showed high performance. The erosion resistance is 1360 – 1500 units.

The corrosion resistance of the coated material was studied at 700, 800, and 900°C under different climatic conditions in a chamber with a salt fog, a chamber with a tropical climate, and in an industrial atmosphere. The results show that as the testing temperature increases from 700 to 900°C the sulfide corrosion rate remains the same level. The experimental results obtained under different climatic conditions show that the thin-film coatings possess high corrosion resistance in tropical and industrial atmospheres and do not decrease the corrosion resistance of the sealing material — Fe(Ni)CrAlY.

The new SiC – Si_3N_4 – SiO_2 high-temperature thin-film coatings which have high oxidation resistance and are based on ceramic-forming polymers can be used to fabricate abradable seals for the flow part of a compressor and turbine in GTE. This will decrease the wear along the ends of expensive blades, which saves fuel because the compressor operates more efficiently, and will increase their service life.

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